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Risk Assessment and Accumulation of Metals in Sediment of Köyceğiz Lagoon System, Turkey

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ABSTRACT

This paper focuses on metal (Cr, Cu, Pb, Mn and Zn) accumulation and degree of contamination in the sediments of the Köyceğiz Lagoon Systems. Pollution by these metals was examined using several calculation methods: pollution load index (PLI), contamination factor (CF), geoaccumulation index (Igeo) and enrichment factors (EF). The mean value of contamination factor (CF) for Pb, Cu, Zn, Mn metals showed low degree of contamination (CF < 1), whereas Cr showed considerably degree (3≤CF< 6). Higher PLI values were observed in sampling sites III where discharge point of waste water and the PLI values indicated that Cr is the major contributors to the sediment pollution. Average Igeo values of analyzed metals (except Cr) indicating uncontaminated to moderately contaminated status of the sediment whereas the Igeo values for Cr indicates moderately to strongly contaminated status. For most of the sites EF of the studied metals were lower than 1 indicating there is not intense human influence to the metal pollution in sediments.

Indexing terms/Keywords

Metal; sediment; pollution load index; contamination factor; geoaccumulation index; enrichment factors; Turkey.

Academic Discipline And Sub-Disciplines

Biology, Environmental toxicology

SUBJECT CLASSIFICATION

Sedimentary Environments

TYPE (METHOD/APPROACH)

Original research work. Metal accumulation in sediments was determined and it was related to several calculation methods (Pollution index, contamination factor, geoaccumulation index and enrichment factor).

INTRODUCTION

In developing countries, rapid increase in domestic, agricultural and industrial activities contribute to elevated levels of metals in the air, water and soil (Sharma et al., 2007; Rahman et al., 2010; Solaraj et al., 2010).

The most important group of pollutants like metals in the environment created the toxicity in proportion to the available amount (Canpolat and Çalta, 2001). Metals are stable and persistent environmental contaminants of aquatic environments (Karadede Akın and Ünlü, 2007) and enter the aquatic environment, soil, and plants from natural and anthropogenic sources (Gümgüm et al., 2001).

Metals often do not constitute the main problem in municipal wastewater because the concentrations of heavy metals are usually low, namely in wastewaters from small municipalities with no industrial effluents (Vymazal et al., 2007; Kröpfelová et al., 2009). However, metals tend to accumulate in sediments; the amount sequestered in the sediments increase with operation time of constructed wetlands (Ranieri and Young, 2012).

In aquatic ecosystems heavy metals are accumulated in sediments, where may reach concentrations several orders of magnitude greater than in the overlying water (Bryan and Langston 1992).

Sediment associated metals pose a direct risk to detrital and deposit-feeding organisms, and may also represent long-term sources of contamination to higher trophiclevels (Mariín-Guirao et al., 2005). Due to the ecological importance and the persistence of pollutants in the aquatic ecosystems, sediments are more appropriate to be monitored in environmental evaluations and understand their potential toxic impacts (Ghrefat and Yusuf, 2006).

Aquatic systems including lagoons, lakes, rivers and inland wetlands are among the most affected systems by metal contamination. Lagoons are known to contain a number of metals at dangerously high level because of metal containing wastes most often disposed there (Genç and Yılmaz, 2015).

Köyceğiz Lagoon System, declared as a Special Protection Area in 1988 (Bayari et al., 1995) is located in south-western of Turkey. The area is composed of terrestrial structures of various qualities around Köyceğiz Subsidence Lake. The lagoon is under pollution pressure of agricultural run-off, untreated urban waste and tourist-boat traffic (Yorulmaz et al., 2015) Intense touristic and agricultural activities and rapid urbanization are prominent cause for environmental deterioration in Köyceğiz lagoon system (Genç and Yılmaz, 2015).

Therefore, regular sediment quality monitoring, with special reference to metal speciation, is necessary as sediments decipher short and long term pollution load (Kwon and Lee, 2001). These metals pose a high environmental risk due to their long time persistence in nature and possible bioaccumulation and bio-magnification (Uysal et al., 2009).

Several studies have reported on metal concentrations in the sediments and the toxicity risk in aquatic organisms (Oglu, 2015; Genç et al., 2015). This study aimed to determine the level of chromium (Cr), copper (Cu), lead (Pb), manganese (Mn) and zinc (Zn) in the sediments; the values for the metal concentrations obtained were used to calculate the pollution load index (PLI), contamination factor (CF), geoaccumulation index (Igeo) and enrichment factor (EF).

MATERIALS AND METHODS

Study area

Lake Köyceğiz, located in southwestern Turkey, is a meromictic lake with a surface area of 55 km2. Impermeable ophiolitic rocks, and groundwater bearing alluvium and karstified limestone are the major geologic units around the lake. Köycegiz lake, fed mainly by rainfall and stream flow, discharges into the Mediterranean Sea via a 14 km long natural channel. The average water level is estimated to be slightly above the sea level and the estimated lake volume is 826 million m^3. Lake level fluctuations are well correlated with rainfall intensity (Bayari et al., 1999). In order to determine the distribution of metal contamination in Koyceğiz Lagoon System sediments, these stations were divided into eight site groups based on the possible touristic, agricultural and anthropogenic activities and showed Figure 1. Station I (Namnam river: agricultural activity), station II (Yuvarlakçay river: agriculture area and fishing village), station III (Water treatment facilities: discharge point of waste water), station IV (Sultaniye thermal water), station V (Middle of the lake), station VI (channel between the river and the sea), station VII (Dalyan: tourist resort and densely populated area), station VIII (channel output region: where close to the sea side).

Fig. 1: Sampling points of Köyceğiz Lagoon System

Sample collection and preparation

A total of 32 sediment samples were collected during September – August 2011 (autumn, winter, spring and summer). Samples were collected from eight different stations (SI–SVIII) from river to sea side of the lagoon.

At each point, composite sediment samples were collected using standard protocol (USEPA, 2001). The sediment samples were taken at a depth of 0 to 5 m using a portable Ekman grab sampler. Three composite samples of mass approximately 200 g were collected at each station. The upper 2 cm of each sample was taken from the center of the catcher with an acid-washed plastic spatula to avoid any contamination from the metallic parts of the sampler.

Sample digestion and metal analyses

The sediments were dried at 105°C for 24 h. The dried sediments were passed through a 60 mesh stainless screen to remove larger particles. Ultrapure (Direct-Q 8UV Germany) water was used for solution preparation. The Teflon vessel were cleaned, soaked in %5 HNO_3 for more than 1 day than rinsed with ultrapure water and dried. For metal analysis, 0.5

g of sediment sample and 20 mL water sample was treated with 7 mL 70 % HNO3 acid and 3 mL 30% H2O2 in a closed Teflon vessel and was digested microwave digestion system (Berghof speedway MWS-3+).

The operating conditions for digestion system are given in Table 1. The digested solution was then filtered by using Filter papers (Sartorius-Stedim, particle retention=2-3µm) and stored in 25 mL polypropylene tubes. Lastly of digestion procedure, the samples were cleaned by ultrapure water and dried with air.

Table 1. Operating conditions for digestion system (MWS-3+)

Stage	1	2	3	4	5
Temperature [^{o}C]	175	100	100	100	100
Pressure [bar]	30	0	0	0	0
Time [min]	10	10	10	10	10
Slope [min]	1	1	1	1	1
Power [%]	80	0	0	0	0

All samples were analysed simultaneously two times for Cr, Cu, Pb, Mn, Zn by ICP-AES Optima 2000-Perkin Elmer (Inductively Coupled Plasma-Atomic Emission Spectrometry). Detection limits (µg l-1) were as follows: Cr (0.007), Cu (0.014), Pb (0.001), Mn, (0.005), Zn (0.006). Standard solutions were prepared from stock solutions (Merck, multi element standard). Standard reference National Water Research Institute WQB1 (for sediment) was analyzed for metals and showed good accuracy, with recovery rates for metals between 92% and 102% for sediment.

RESULT AND DISCUSSION

The Pollution load index (PLI)

The Pollution load index (PLI) was proposed by Tomlinson et al., (1980) for detecting pollution which permits a comparison of pollution levels between sites and at different times. In this study, the world average concentrations of the metals studied reported for shale (Martin and Meybeck, 1979) were used as the background for those metals. PLI is able to give an estimate the metal contamination status and the necessary action that should be taken (Amin, 2009). The PLI is defined as the nth root of the multiplications of the contamination factor of metals (CF).

$$\text{Contamination factor (CF)} = \frac{\text{Metal concentration in sediment}}{\text{Background value of the metal}}$$

PLI is expressed as: PLI = $(CF_1 \times CF_2 \times CF_3 \times \ldots\ldots\ldots\ldots \times CFn)^{1/n}$

Where, n is the number of metals (six in the present study) and CF is the contamination factor. The ratio of the measured concentration to natural abundance of a given metal had been proposed as the index contamination factor (CF) being classified into four grades for monitoring the pollution of one single metal over a period of time (Turekian and Wedepohl, 1961; Loska et al., 1997): low degree (CF < 1), moderate degree (1≤CF < 3), considerable degree (3≤CF < 6), and very high degree (CF≥6). Thus the CF values can monitor the enrichment of one given metal in sediments over a period of time (Islam 2015).

The results of CF in sediment of the lagoon Köyceğiz are shown in figure 2. The CF for all metals were the descending order of Cr>Mn>Cu>Zn>Pb. The mean CF values of Cr, Pb, Cu, Zn and Mn were 4.3, 0.65, 0.89, 0.53 and 0.83 during autumn, 7.49, 0.48, 1.1, 0.44 and 1.18 during winter, 3.43, 0.27, 0.76, 2.09 and 0.78 during spring and 5.47, 0.29, 0.95, 0.16 and 1.13 during summer. The value of contamination factor (CF) on autumn for Pb, Cu, Zn, Mn metals showed low degree of contamination (CF < 1), whereas Cr showed considerably degree (3≤CF< 6). CF values on autumn similar with other seasons but Cu and Zn on winter, Zn on spring and Mn on summer showed moderate degree (1≤CF < 3). This result show that agricultural inputs in summer were probably the major contributor for Köyceğiz Lagoon System.

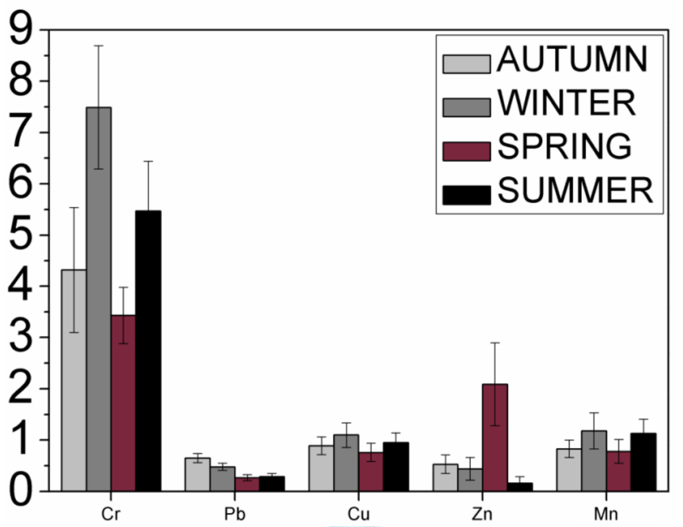


Fig. 2: Contamination factor (CF) of metals in sediment

The assessment of pollution load index (PLI) distribution among the eight site groups can be seen in figure 3. The pollution load index (PLI) values of metals in sediment were ranged from 0.04 to 4.63 during autumn, 0.01 to 18.63 during winter, 0,01 to 8.45 during spring and 0.01 to 6.74 during summer. However, the higher PLI values indicated that Cr is the major contributors to the sediment pollution. The PLI can provide some understanding to the inhabitants about the quality of the environment. In addition, it also provides valuable information to the decision makers on the pollution status of the area (Suresh et al., 2012). Higher PLI values were observed in sampling sites SIII, which might be due to the effects of discharge of waste water. Lower PLI values in sites V and VI were observed, probably due to low anthropogenic activities in the area. No industrial activities take place in these sites. PLI values in Rivers (Station I and II) show that any developed cities different kind of wastes are introduced in to the river system,which has often led to a significant impact on quality of the aquatic ecosystem and its metal concentrations especially in sediments (Buckley et al., 1995; Li et al., 2000).

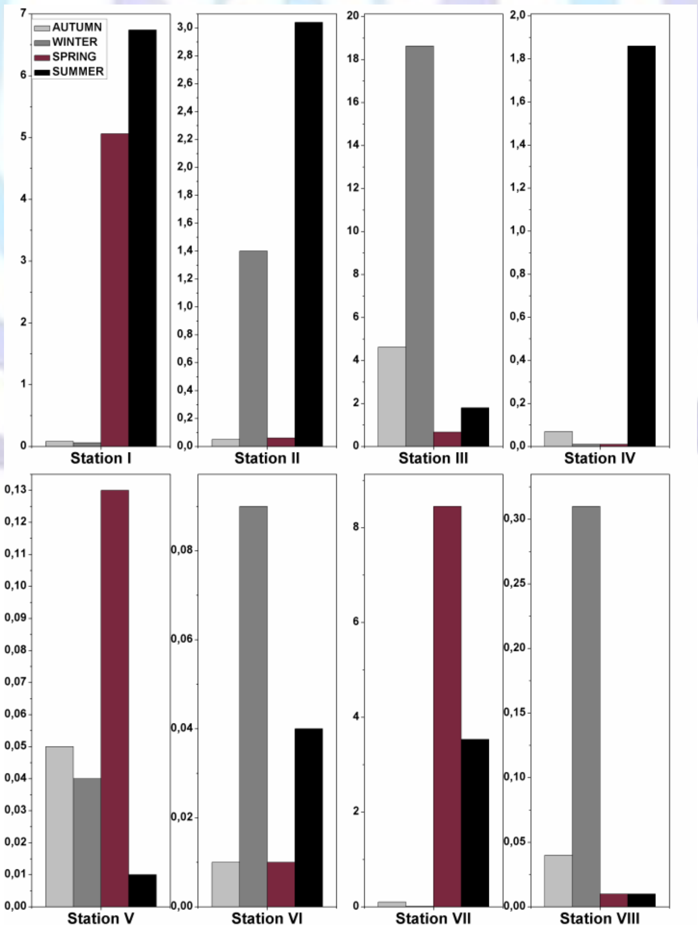


Fig. 3: Pollution load index (PLI) value in sediment

Geoaccumulation Index (*Igeo*)

The geoaccumulation index (Igeo), introduced by Muller (1979) for determining the extent of metal accumulation in sediments, and has been used by various workers in their studies (Rath et al., 2005; Likuku et al., 2013; Islama, 2015).

$$Igeo = \text{Log}2[\frac{Cn}{1.5Bn}]$$

Where Cn is the measured concentration of metal n in the sediment and Bn is the geochemical background value of element n in the background sample. The factor 1.5 is introduced to minimize the possible variations in the background values which may be attributed to lithogenic effects. The index of geoaccumulation was assessed based on the seven descriptive classes for increasing Igeo values proposed by Müller (1979), depicted in Table 2.

Table 2. Descriptive classes for Igeo values

Value	Class	Description
Igeo>5	6	Extremely contaminated
4< Igeo<5	5	Strongly to extremely contaminated
3< Igeo<4	4	Strongly contaminated
2< Igeo<3	3	Moderately to strongly contaminated
1< Igeo<2	2	Moderately contaminated
0< Igeo<1	1	Uncontaminated to moderately contaminated
Igeo=0	0	Uncontaminated

Figure 4 presents the geoaccumulation factor (Igeo) values of the studied metals. Among the studied metals, the Igeo values showed the decreasing order of Cr>Mn>Cu>Zn>Pb. Pb, Cu, Zn and Mn were 0.09 to 0.69, 0.24 to 1.35, 0.13 to 0.96 and 0.25 to 1.34 during autumn and 0.19–0.71, 0.37 to 1.38, 0.07 to 1.98 and 0.41 to 1.36 during winter, 0.04 to 0.39, 0.39 to 1.57, 0.0 to 7.51 and 0.0 to 1.96 during spring and 0.2 to 6.25, 0.44 to 1.01, 0.02 to 7.87 and 0.39 to 2.97 during summer; average Igeo values of these metals indicating uncontaminated to moderately contaminated status of the sediment whereas, the Igeo values for Cr 2.30 to 12.7, 3.45 to 13.09, 1.56 to 5.79 and 2.62 to 11.21 during autumn, winter, spring and summer season, respectively. Average Igeo values of Cr for autumn and spring indicates moderately to strongly contaminated status while Cr for summer showed strongly contaminated status which might be due to the higher concentration in sediment and lower level in the background sample. Essential metals like Mn, Zn, Cu and Cr play a major role in the biological activities of marine organisms, and non- essential metals like Pb are the most toxic elements. Even essential metals may be toxic for the biological activities of organisms above certain concentrations (Merciai et al., 2014).

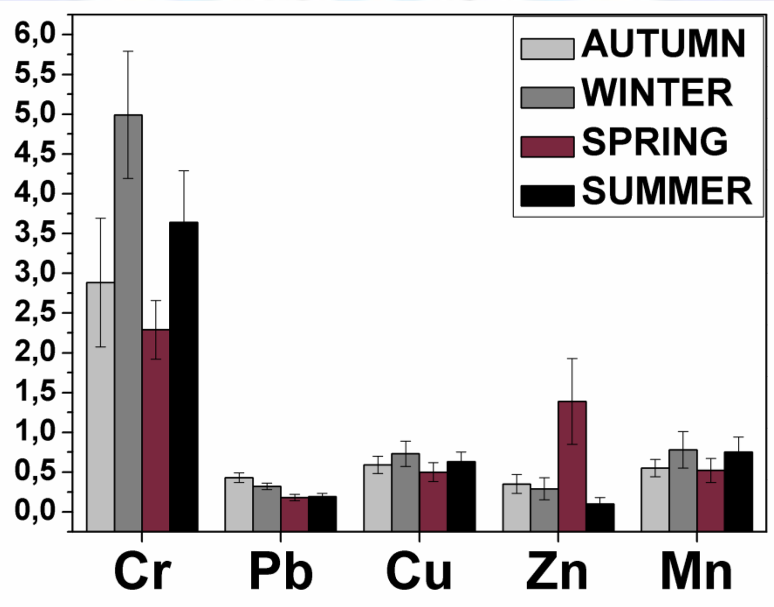


Fig. 4: Geoaccumulation index (Igeo) value of metals in sediment

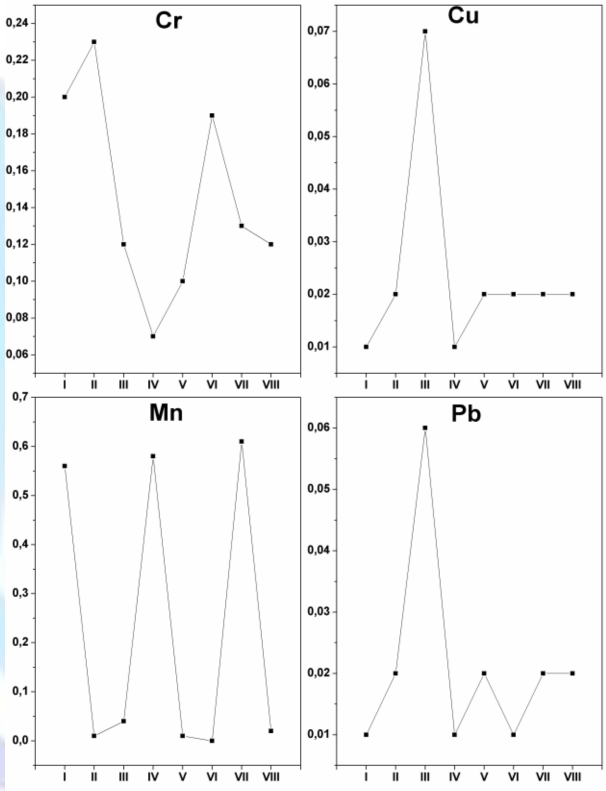
Enrichment factor (EF)

Enrichment factor (EF) is a normalization technique widely used to categorize the metal fractions that is associated with sediments. EF represents the actual contamination level in the sediment (Groengroeft et al., 1998) and is a good tool to differentiate the metal source between anthropogenic and naturally occurring (Morillo et al., 2004; Selvaraj et al., 2004; Valdés et al., 2005).

According to Ergin et al., (1991), the metal EF is defined as follows

$$\text{Enrichment Factor (EF)} = \frac{(Cx/Fe)\text{sample}}{(Cx/Fe)\text{background}}$$

EF values were interpreted as suggested by Birch (2003) where EF < 1 indicates no enrichment, < 3 is minor; 3-5 is moderate; 5-10 is moderately severe; 10- 25 is severe; 25-50 is very severe; and > 50 is extremely severe. Enrichment factor (EF) is a normalization technique widely used to categorize the metal fractions that is associated with sediments (Islama, 2015). Figure 5 showed the mean EF values of the metals studied.



(The average EF for Zn were = 0.01 at all station and not represented on figure)

Fig. 5: Enrichment factor (EF) values for metals in sediments of sampling sites

EF values for all metals at all station were <1 indicated no enrichment of these metals. In an unpolluted environment, metal are attached to silicate and minerals. However, under anthropogenic induced environmental stress, metals may occur in such labile forms as oxides, hydroxides, carbonates, sulfides etc. and may join the liquid matrix (water). Hence, sediment may behave as source and sink of metals (Passos et al., 2010; Medici et al., 2011). For most of the sites EF of the studied metals were lower than 1 indicating there is not intense human influence to the metal pollution in sediments.

CONCLUSION

It is presumed that high PLI values on SI and S III indicate an anthropogenic source of metals, mainly from activities such as agricultural and waste water treatment.

Large amounts of discharge in agricultural waste may cause significant and rapid environmental changes results in environmental deterioration in this bay.

The overall pollution load was significantly higher in summer than other seasons.

The contamination factor (CF) and geoaccumulation index (Igeo) revealed that sediments in this study were considerably polluted by Cr and moderately polluted by other metals.

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